ELASTIC SCATTERING OF SLOW ELECTRONS FROM ALKALI ATOMS*†

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ABSTRACT

The elastic scattering cross sections for slow electrons incident on sodium and potassium are calculated using a model for the polarization potential which was earlier used for cesium. In all the alkalis studied, the low energy scattering cross sections show an extreme sensitivity to the exact shape of the polarization potential in the region where r is comparable to the atomic radius, indicating the necessity of having an accurate description of the polarization term in the total scattering interaction potential. An attempt is made to derive the polarization potential applicable to the low energy collision problem, and calculations are made for electron - cesium atom collisions. It is found that the derived polarization potential has general features similar to those of the model. The results are compared with the available experimental data.

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Introduction

In a previous paper[1] a model was proposed to include the polarization potential in the total interaction potential for the scattering of slow electrons by cesium atoms. The method used was similar to that of Robinson[2] except in the form assumed for the polarization term. In the first part of the present paper we extend the use of this model to the scattering of electrons by other alkali atoms. We have found that the low energy scattering cross sections, for all the alkalis studied, show an extreme sensitivity to the exact shape of the polarization potential in the region where r is comparable to the atomic radius. It would thus be desirable to be able to calculate a polarization potential for the low energy atomic collision problem which is accurate for all values of r. A number of calculations for electron - hydrogen collisions have been made[3], and a polarization potential for helium has been calculated by O'Bedkov [4]. However, for heavier atoms, few investigations have been made of the polarization potential. Callaway[5] has calculated polarization potentials for the core electrons of alkali metals, and in a recent paper Stone and Reitz[6] have obtained the polarization potential for electron cesium atom collisions in their analysis of low energy electron scattering. In their calculation, only the contribution from the population of the 6p level was included in the polarization potential. At small radii other contributions can become important in the calculated polarization potential and should be included.

In the second part of the present investigation we make use of the adiabatic model, in which the atomic system is assumed to polarize in response to the instantaneous position of the incident particle, and first order perturbation theory to derive the dipole polarization potential for a charged particle in the field of an atom. The analysis, which is similar to that used by Reeh[7] for determining the polarization of the core electrons for hydrogen-

like ions is then applied to the cesium atom to obtain the polarization potential for the electron scattering problem.

I. Model for the Scattering of Slow Electrons from Alkali Atoms.

A. Method of Solution

The elastic scattering cross sections for potassum and sodium were obtained in exactly the same matter as that described in I. The model for the effective scattering potential consists of the Hartree potential function for the neutral alkali to which a polarization term of the form

$$V_p(r) = \frac{\alpha}{2r^4}\left\{1 - \exp\left[-\left(\frac{r}{fr_o}\right)^8\right]\right\} \tag{1}$$

is added, where α is the experimental polarizability for the atom in question and the quantity $f\,r_o$ is the so called cut off parameter. The complete interaction potential which appears in the scattering equation is then

$$V(r) = V_H(r)/r + \left(\alpha/2r^4\right)\left(1 - \exp\left[-\left(\frac{r}{fro}\right)^8\right]\right) \tag{2}$$

where $V_H(r)/r$ is the Hartree potential function. In the present calculations the Hartree potential $V_H(r)$ for potassium was taken from the results of Hartree[8] and of Gibbons and Bartlett[9], and for sodium the potential function of Fock and Petrashen[10] was used.

The constant r_o was again taken as the position of the last maximum of the valence electron wave function ($r_o = 5.0\ a_o$ for K, and $r_o = 3.5\ a_o$ for Na) and the parameter f was varied over a small range near f = 1.0. Two different values of the polarizability from the literature[11] were used for each case; $\alpha = 36$ Å^3, 45 Å^3 (248, 326 a_o^3) for potassium and $\alpha = 24$, 27 Å^3 (161, 182 a_o^3) for sodium.

B. Results for K and Na.

The total elastic scattering cross sections for K and Na were obtained by the phase shift method (neglecting enchange) as described in I. It was found that the cross sections for both atoms were extremely sensitive to the shape of the polarization potential as determined by varying the parameter f in eq. (1). This same result was found previously for Cs[1]. We note that a change in the cut off parameter fr_o changes the position and magnitude of the maximum in the polarization term V_p, this maximum lying near the position of the last maximum of the valence electron wave function for the atom in question (Fig. 1 of I).

In Figs. 1 and 2 we have plotted the results for K and Na which best fit the experimental values of Brode[12], and of Perel, Englander and Bederson[13]. We see that the present model yields results which are in good agreement with the experimental results. We will say more in the last section about the conclusions which can be drawn from the use of the present model.

II. Theoretical Development of the Polarization Potential.

A. Formulation of the Problem

We will consider a free electron incident on an unbound, stationary atom. If we let r_f denote the position vector of the free electron and r_i that of one of the bound atomic electrons, then the total Hamiltonian for the system can be written:

$$H = H_a(\bar{r}) + H_f(\bar{r}_f) + W(r, r_f) \tag{3}$$

where

$$W(r, r_f) = \sum_i \frac{1}{|\bar{r}_i - \bar{r}_f|} . \tag{4}$$

In this decomposition $H_a(r)$ is the Hamiltonian of the unperturbed atom, $H_f(\bar{r}_f)$ is that of the free electron, and $W(r, r_f)$ is the interaction of the

free electron with the atomic electrons. Considering first the case of a hydrogen like atom or ion we write the total wave function $\Psi(\bar{r},\bar{r}_f)$ for the system in the form

$$\Psi(\bar{r}, \bar{r}_f) = \Phi(\bar{r}, \bar{r}_f) \quad \psi(\bar{r}_f) \quad . \tag{5}$$

Here $\Phi(\bar{r}, \bar{r}_f)$ describes the target atom, and $\psi(r_f)$ describes the free electron. The complete wave function $\Psi(\bar{r}, \bar{r}_f)$ has not been antisymmetrized here, thus in the present calculation the effect of electron exchange on the polarization potential will be neglected. This is consistant with the use of Hartree wave functions to describe the unperturbed atom. The wave function for the perturbed atomic electron is now written as

$$\Phi(\bar{r}, \bar{r}_f) = \Phi_o(\bar{r}) + \chi(\bar{r}, \bar{r}_f) \tag{6}$$

where $\Phi_o(r)$ is the unperturbed wave function for the atomic electron and satisfies

$$H_a(\bar{r})\ \Phi_o(\bar{r}) = E_o\ \Phi_o(r)$$
$$\langle \Phi_o\ ,\ \Phi_o \rangle = 1 \tag{7}$$

and $\chi(\bar{r}, \bar{r}_f)$ is first order perturbation of the orbital electron wave function. In addition we require that $\langle \Phi_o, \chi \rangle = 0.$ (8)

In this representation the Schroedinger equation for atomic scattering is

$$[H_a(\bar{r}) + H_f(\bar{r}_f) + W(r,r_f)] \left(\Phi_o(\bar{r}) + \chi(\bar{r},\bar{r}_f)\right) \psi(\bar{r}_f)$$
$$= E \left(\Phi_o(\bar{r}) + \chi(\bar{r},\bar{r}_f)\right) \psi(\bar{r}_f). \tag{9}$$

The polarization potential in the total interaction of free electron and atomic system can be obtained by performing a scaler multiplication from the left on eq. (9) above and make use of equations (7) and (8). Thus

$$(E - E_o)\langle \psi, \psi \rangle = \langle \psi, H_f \psi \rangle + \langle \psi, \langle \Phi_o, W\ \Phi_o \rangle\ \psi \rangle + \langle \psi, \langle \Phi_o, W\ \chi \rangle\ \psi \rangle \tag{10}$$

Looking at the last two terms on the right side of eq. (10) the second

term can be identified as the mutual interaction energy of the free electron with the atomic electron and the third term represents the mutual interaction of the free electron with the perturbation of the atomic wave function; this then is the polarization energy. We thus make the identification:

$$V_p(r_f) = \langle \Phi_o, W \chi \rangle \tag{11}$$

where $V_p(r_f)$ is the polarization potential seen by the free particle due to the distortion of the target atom.

A differential equation for the determination of the perturbation, χ, can be obtained from the Schroedinger eq. (11) describing the scattering process. After obtaining the expression for E from eq. (10) and substituting in equation (9) and rearranging the equation becomes:

$$\begin{aligned}(H_a + W)(\Phi_o + \chi)\Psi + (H_f \chi - \chi H_f)\Psi \\ = \left[E_o + \langle \Phi_o, W\Phi_o \rangle + \langle \Phi_o, W\chi \rangle\right](\Phi_o + \chi)\Psi .\end{aligned} \tag{12}$$

At this point a simplification of the equations can be affected by making use of the adiabatic approximation which was mentioned earlier. The polarization of the orbital electron is considered as taking place in the static field of the slow incident particle. The dynamic equation above, which determines the distortion of the atomic orbital and also the effect of this distortion on the external electron, is thus replaced with the static problem. This is done simply by fixing r_f in eq. (12), causing the second term on the left side to disappear. The equation then becomes:

$$\begin{aligned}\left[H_a(r) + W(r,r_f)\right]\left(\Phi_o(\bar{r}) + \chi(\bar{r},\bar{r}_f)\right) = \left[E_o + \langle \Phi_o, W \Phi_o \rangle\right. \\ \left. + \langle \Phi_o, W \chi \rangle\right]\left(\Phi_o(\bar{r}) + \chi(r,r_f)\right)\end{aligned} \tag{13}$$

We now consider the interaction $W(r,r_f)$ as a perturbation on the unperturbed system which satisfies eq. (7), the solutions of which are considered

known. If we consider this term small as compared to $H_a(r)$ and keep only terms through first order in the perturbation χ, eq. (13) is greatly simplified. With this approximation and the use of eq. (7), the above equation becomes:

$$\left[H_a(r) - E_o \right] \chi(\vec{r}, \vec{r}_f) = \left[\langle \Phi_o, W\Phi_o \rangle - W(\vec{r}, \vec{r}_f) \right] \Phi_o(\vec{r}) \qquad (14)$$

This is an inhomogeneous differential equation for the determination of the function $\chi(r, r_f)$. This was solved by Ob"Edkov[4] through a variational technique for hydrogen and helium in their ground state, and analytically by Reeh[7] for hydrogen and hydrogen-like ions.

B. The Hartree Approximation for a Many Electron Atom

For a multi-electron atom an analysis somewhat similar to the Hartree separation of the atomic electron wave functions (without exchange) may be used to obtain a polarization potential. Let us replace the Hamiltonian for the complete atom

$$H_a(r) = \sum_i \left(-\tfrac{1}{2} \nabla_i^2 - Z/r_i \right) + \tfrac{1}{2} \sum_{i \neq k} \frac{1}{r_{ik}}$$

with a separated operator of the form

$$H_a(r) = \sum_i H_i(\vec{r}_i)$$

where $H_i(r_i)$ depends only on the coordinates of the i^{th} electron and the average effect of the other electrons. The wave function for the atom is similarly separated in the form

$$\Phi_o(r) = \varphi_1(r_1)\, \varphi_2(r_2) \cdots \varphi_n(r_n)$$

and

$$H_i \varphi_i = E_i \varphi_i \quad . \qquad (15)$$

Finally, the complete wave function is written

$$\Phi_o + \chi = (\varphi_1 + \chi_1)(\varphi_2 + \chi_2) \cdots (\varphi_n + \chi_n)$$

with

$$\langle \varphi_i, \chi_i \rangle = 0 \quad ; \quad \langle \varphi_i, \varphi_i \rangle = 1 \qquad (16)$$

With this approximation the first order equation (14) becomes, in the multielectron case,

$$\left[H_i - E_i \right] \chi_i \ (\bar{r}_i, \bar{r}_f) = \left[\left\langle \varphi_i, w_i \varphi_i \right\rangle - w_i \right] \varphi_i(r_i) \tag{17}$$

Where

$$W = \sum_i w_i \quad ; \quad w_i = \frac{1}{|\bar{r}_f - \bar{r}_i|} \ .$$

This is an inhomogeneous differential equation for the perturbation χ_i of the single electron orbital φ_i of the complete atom. The polarization potential for the complete atom is then

$$\begin{aligned} V_p(r_f) &= \sum_i \int \varphi_i \, w_i \, \chi_i \, d^3 r_i \\ &= \sum_i V_{p_i}(r_f) \end{aligned} \tag{18}$$

where

$$V_{p_i}(r_f) = \int \varphi_i \, w_i \, \chi_i \, d^3 r_i \tag{19}$$

Thus in this approximation the polarization potential for a many electron atom may be calculated by considering the contribution due to each of the various orbitals, which may be known Hartree solutions for the atom in question.

C. The Radial Equations

The inhomogeneous equations (14) or (17) for the perturbation χ can be separated and radial equations for the various angular momentum states written.

(1) The Dipole Approximation

Returning to eq. (17) we write it in a more explicit form. For the i^{th} electron we get:

$$\left[-\tfrac{1}{2} \nabla_i^2 + V(r_i) - E_o \right] \chi_i(r_i, r_f) = \left[\int \phi_i^* \frac{1}{r_{if}} \phi_i \, d^3 r_i - \frac{1}{r_{if}} \right] \phi_i(r_i) \tag{20}$$

We choose a coordinate system in which the z-axis is oriented parallel

to the position vector r_f of the free electron. In this system we make use of the usual expansion

$$\frac{1}{r_{if}} = \sum_{\lambda=o} \left(\frac{4\pi}{2\lambda+1}\right)^{\frac{1}{2}} \frac{r_<^\lambda}{r_>^{\lambda+1}} Y_\ell^o(\theta,o) \qquad (21)$$

$$= \frac{1}{r_<} + \frac{r_<}{r_>^2} \cos\theta + \frac{r_<}{2r_>^3} (3\cos^2\theta - 1) + \ldots .$$

where $r_<$ is the lesser and $r_>$ the greater of r_i and r_f. In this expansion the term in $\cos\theta$ gives the dipole potential, the $(3\cos^2\theta - 1)$ term gives the quadrupole and so on. We will drop the quadrupole and higher order terms in the expansion above and keep only the first two terms in the $1/r_{if}$ series.

If we now substitute the expansion (21) for the $1/r_{if}$ term in the intergral on the right side of eq. (20), all but the spherically symmetric term vanish. With this result the two terms in the brackets on the right side of (20) become:

$$\left[1/r_f \int_o^{r_f} \phi_i^* \phi_i \, d^3 r_i + \int_{r_f}^{\infty} \phi_i^* \frac{1}{r_i} \phi_i \, d^3 r_i - \frac{1}{r_<} - \frac{r_<}{r_>^2} \cos\theta \right]$$

We note that for large values of r_f the first term in the bracket above goes to $1/r_f$ and the second term goes to zero. This first term then cancels the third leaving only $\frac{r_<}{r_>^2} \cos\theta$ which is the dipole term, the monopole term having vanished. For small values of r_f the monopole term does contribute of course, but it goes to zero exponentially for large r_f. For smaller values of r_f, where the monopole contribution is appreciable the coulomb potential of the partially shielded nucleus becomes large, and tends to mask this term. We will thus make the "dipole approximation" at this point and consider only the last term in the brackets above, that is, the dipole contribution in the total polarization potential. We then have the equation

for the perturbed wave χ_i in the form:

$$\left[-\tfrac{1}{2}\nabla_i^2 + Z(r_i)/r_i - E_o \right] \chi_i(r_i, r_f) = -\frac{r_<}{r_>^2} \cos\theta \, \phi_i(r_i) \tag{22}$$

which is actually the two equations

$$\left[-\tfrac{1}{2}\nabla_i^2 + Z(r)/r_i - E_o \right] \chi_i(r_i, r_f) = -\frac{r_i}{r_f^2} \cos\theta \, \phi_i(r_i) \qquad (r_f > r_i)$$

$$\left[-\tfrac{1}{2}\nabla_i^2 + Z(r_i)/r_i - E_o \right] \chi_i(r_i, r_f) = -\frac{r_f}{r_i^2} \cos\theta \, \phi_i(r_i) \qquad (r_f < r_i) \tag{23}$$

These equations can be solved for the perturbed wave χ_i where the solutions to (23) must be joined at the boundary $r_i = r_f$. The dipole polarization potential integrals to be evaluated are:

$$V_p(r_f) = \sum_i \left\{ \frac{1}{r_f^2} \int\int_o^{r_f} \phi_i^*(r_i) r_i \cos\theta \, \chi_i(r_i, r_f) \, d\vec{r}_i \right.$$
$$\left. + r_f \int\int_{r_f}^{\infty} \phi_i(r_i) \frac{\cos\theta}{r_i^2} \chi_i(r_i, r_f) \, dr_i \right\} \tag{24}$$

(2) Contributions from the Various Angular Momentum States

We will consider individually the perturbations of electron orbitals of angular momentum $\ell = 0, 1, 2$. We write the unperturbed wave functions in the form

$$\Phi_o(r) = R_{n\ell}(r) \, Y_\ell^m(\theta, \phi) = \frac{P_{n\ell}(r)}{r} \, Y_\ell^m(\theta, \phi) \tag{25}$$

where $P_{n\ell}(r) = r \, R_{n\ell}(r)$ is the reduced radial function. We also expand the perturbation χ in the form:

$$\chi(\vec{r}, \vec{r}_f) = \sum_k \sum_{|m'| < k} X_{k',m'}(r, r_f) \, Y_{k'}^{m'}(\theta, \phi) \left(\frac{4\pi}{2k'+1} \right)^{\frac{1}{2}} . \tag{26}$$

For convenience let us make the further variable changes

$$X_{k',m'}(r,r_f) = \frac{U_{k',m'}(r,r_f)}{r} \tag{27}$$

and $\quad 2E_o = -\epsilon$.

With these variables the general differential equation (22) then becomes:

$$\sum_{k'} \sum_{|m'|<k'} \left(\frac{d^2}{dr^2} - \frac{k'(k'+1)}{r^2} + \frac{2Z(r)}{r} - \epsilon \right) \sqrt{\frac{4\pi}{2k'+1}}\, U_{k',m'}(r,r_f)\, Y^{m'}_{k'}(\theta,\phi)$$

$$= \frac{2r_<}{r_>^2} \sqrt{\frac{4\pi}{3}}\, Y^o_1(\theta,o)\, P_{n,\ell}(r)\, Y^m_\ell(\theta,\phi) \tag{28}$$

where the cosθ term on the right side of (22) has been written as a spherical harmonic and $P_{n\ell}(r)\, Y^m_\ell(\theta,\phi)$ are the appropriate radial and angular functions for the unperturbed state in question. The index i has been dropped from the bound electron coordinate for convenience.

The appropriate radial equations for the perturbation χ of an orbital $\bar{\Phi}_o$ are obtained by performing a scalar multiplication from left on equation (28) with $Y^{m_1 *}_{k_1}(\theta,\phi)$.

(9) s-states

We consider the case where the unperturbed electron is in an s-state. In this case

$$\Phi_o(r) = \frac{P_{n\ell}(r)}{r}\, Y^o_o(\theta,\phi) \ . \tag{29}$$

The before mentioned scalar multiplication of equation (28) leads in this case

to the single radial equation

$$\left[\frac{d^2}{dr^2} + 2\frac{Z(r)}{r} - \frac{2}{r^2} - \epsilon\right] U_{1,o}(r,r_f) = \frac{2r_<}{r_>^2} P_{no}(r) \frac{1}{\sqrt{4\pi}} . \qquad (30)$$

The solution to this equation with equation (26) and (27) gives

$$\chi_{o\to 1}(r,r_f) = \frac{U_{1,o}(r,r_f)}{r} \quad Y_1^o(\theta,\phi)\sqrt{\frac{4\pi}{3}} \qquad (31)$$

which is the perturbation of an s-state atomic electron. We note that the perturbed wave has p-character, and thus corresponds to the excitation of the n-s orbital in question to a p-orbital. The notation used to designate the perturbed wave is that of Sternheimer[14]; the symbol $0\to 1$ means a state with $\ell = 0$ going to an $\ell = 1$ perturbed state. In general the notation $\ell \to \ell'$ will indicate an orbital whose unperturbed character is ℓ being perturbed in such a way that the perturbed wave χ has ℓ' character.

The polarization potential as contributed by an s-electron is obtained by substituting the solution (31) in the integral (24).

(b) p-states

For p-states we have $\ell=1$ with m=1, 0, -1. We write the unperturbed p-function in the form

$$\underset{\sim}{\Phi}_o(r) = \frac{P_{n,1}(r)}{r} \quad Y_1^m(\theta,\phi). \qquad (m = \pm 1, o) \qquad (32)$$

Consider first the p-state with m=0. Carrying out the same scalar multiplication as before on eq. (28), the right side vanishes unless $m_1=0$, $k_1=0$, 2, therefore we get two equations for the m=0 p-states. Thus for $k_1=0$:

$$\left[\frac{d^2}{dr^2} + \frac{2Z(r)}{r} - \epsilon \right] U_{o,o}(r,r_f) = \frac{r_<}{r_>^2} P_{n1}(r) \frac{1}{\sqrt{3\pi}} \tag{33}$$

The perturbed wave from this equation is then

$$\chi_{1\to o}(r,r_f) = \frac{U_{o,o}(r,r_f)}{r} Y_o^o(\theta,\phi) \sqrt{4\pi} \tag{34}$$

Where the notation $1\to 0$ indicates a P to S transition since the perturbed wave has s-character. Similarly for $k_1 = 2$ we get:

$$\left[\frac{d^2}{dr^2} - \frac{6}{r^2} + 2\frac{Z(r)}{r} - \epsilon \right] U_{2,o}(r,r_f) = \frac{r_<}{r_>^2} P_{n1}(r) \frac{2}{\sqrt{3\pi}} \tag{35}$$

Thus for a p-state with m = 0 we also have the perturbation contribution

$$\chi_{1\to 2}(r,r_f) = \frac{U_{2,o}(r,r_f)}{r} Y_2^o(\theta,o) \sqrt{\frac{4\pi}{5}} \tag{36}$$

This indicates a $p \to d$ transition since the perturbed wave has d character.

For the p-state with $m = \pm 1$ the scalar multiplication of eq. (28) yields a contribution for $k_1 = 2$, $m = \pm 1$. The radial equation for the perturbation of a p-state with $m = \pm 1$ is then:

$$\left[\frac{d^2}{dr^2} - \frac{6}{r^2} + 2\frac{Z(r)}{r} - \epsilon \right] U_{2,\pm 1}(r,r_f) = \frac{r_<}{r_>^2} P_{n,1}(r) \frac{1}{\sqrt{\pi}} \tag{37}$$

We note that this equation is identical to equation (34) apart from a constant $\frac{2}{\sqrt{3\pi}}$.

The perturbed wave for a p-orbital with m = $\pm$1 is then written

$$\chi_{1\to 2}(\bar{r},\bar{r}_f) = \frac{U_{2,\pm 1}(r,r_f)}{r} \quad Y_2^{\pm 1}(\theta,\phi)\sqrt{\frac{4\pi}{5}} \quad . \tag{38}$$

The contribution to the polarization potential from p-electrons is then obtained by substituting the perturbations (33) and (35) in the polarization integral (24), summing and multiplying by two, since there are two p-electrons with m = 0, and likewise substituting the perturbation (37) for m=$\pm$1 states multiplying by four and adding this to the m=0 contribution since there are four electrons in the m=$\pm$1 states. This then gives the total polarization potential contributed by p-electrons.

(c) d-states

Considering the d-states we have ℓ =2, m= $\pm$2, $\pm$1, 0. The unperturbed wave function is written in the form

$$\Phi_o(r) = R_{n,2}(r)\, Y_2^m(\theta,\phi) \qquad (m= \pm 2, \pm 1, 0) \tag{39}$$

With this expression for Φ_o , the scalar multiplication of equation (28) with $Y_{k_1}^{m_1}(\theta,\phi)$ leads to equations for values of k_1 = 1, m_1 = 0, $\pm$1 and k_1=2 until m_1 = 0, $\pm$1, $\pm$2, corresponding to the following modes of excitation.

d $\rightarrow$ p	m = 0, $\pm$1
d $\rightarrow$ f	m= 0, $\pm$1, $\pm$2

The solutions to these equations, which are similar to those above, along with the angular functions yield the perturbations $\chi_{2\to1}(\bar{r},\bar{r}_f)$ for m = 0, and ±1, and $\chi_{2\to3}(\bar{r},\bar{r}_f)$ for m=0, ±1 and ±2. The total polarization potential as contributed by d-electrons are similarly obtained by integrating the corresponding polarization integrals for each state and multiplying by the number of electrons in that state.

The total polarization potential for an atomic system is finally obtained by adding together the contributions from each of the states considered.

III. Results for Cesium

The formalism of the previous section for the calculation of the polarization potential in the atomic scattering problem was applied to the case of low energy electron-cesium atom collisions.

A. Method of Solution

Let us note first that all the radial equations for the various angular momentum states with a change of variable of the form

$$U_{\ell,m}(r,r_f) = A^m_\ell \; W_{\ell,\ell'}(r,r_f) \tag{38}$$

can be put in the form

$$\left[\frac{d^2}{dr^2} - \frac{\ell'(\ell'+1)}{r^2} + \frac{2\,Z(r)}{r} - \epsilon\right] W_{\ell,\ell'}(r,r_f) = \frac{r_<}{r_>^2}\, P_{n\ell}(r) \,. \tag{39}$$

Here A^m_ℓ is the appropriate constant for the radial equation in question. We

will consider the solutions to eq. 39 for the cesium atom.

For the present calculation, the ordinary Hartree wave functions for cesium were used for the unperturbed system. With these functions, the equations (39) were solved for the perturbations χ, and the polarization integrals evaluated for states appropriate for the cesium problem. In equation, (39) $P_{n\ell}(r)$ is the reduced radial wave functions from the Hartree calculation for a given shell n, with angular momentum ℓ. The quantity ϵ is the eigevalue from the Hartree solution for the given n, ℓ orbital and $\frac{Z(r)}{r}$ is the Hartree potential function.

The radial equations for the perturbations χ_i were intergrated numerically using an inward method of integration starting at a large radius r_1. For this purpose equation (39) was written in a form similar to that used by Sternheimer[14]. That is, we write:

$$\frac{d^2}{dr^2} W_{\ell,\ell'}(r,r_f) = G\, W_{\ell,\ell'}(r,r_f) \tag{40}$$

Where the term G is given by

$$G(r) = \frac{\ell'(\ell'+1)}{r^2} - \frac{2z(r)}{r} + \epsilon + \frac{r_f}{r^2} \frac{P_{n\ell}(r)}{W_{\ell,\ell'}(r,r_f)} \tag{41}$$

It was assumed that G is constant for $r > r_1$, which means that for a given value of $W_{\ell,\ell'}(r_1, r_f)$, the value at $r_1 + \delta$, where δ is the increment size on r, can be calculated from

$$W_{\ell,\ell'}(r_1+\delta, r_f) = W_{\ell,\ell'}(r_1, r_f) \quad \exp[-\sqrt{G(r_1)}\,\delta] \tag{42}$$

the value of $G(r_1)$ having been previously obtained from (41). The numerical integration was thus started by choosing a value of $W_{\ell,\ell'}(r_1, r_f)$ and calculating the value of $W_{\ell,\ell'}(r, +\delta, r_f)$ from (42). With these starting values, the equation for $r > r_f$ was integrated inward to $r = r_f$ where the solution to the equation for $r < r_f$ was matched and the integration continued inward to the orgin. This procedure was repeated for several values of $W_{\ell,\ell'}(r_1, r_f)$. The correct starting value at the large radius r_1 is that for which the solution goes to zero at the origin. To see that this should be the case, we look at the different equation (39) for $r < r_f$. We note that near the origin the term on the right side goes to zero as $r^{\ell+2}$ since $P_{n\ell}(r)$ goes as $r^{\ell+1}$ near the origin. Thus the solution to the inhomogeneous equation (39) near the origin is proportional to that of the homogeneous equation

$$\left[\frac{d^2}{dr^2} - \frac{\ell'(\ell'+1)}{r^2} + 2\frac{z(r)}{r} - \epsilon \right] W_{\ell,\ell'}(r, r_f) = 0$$

But this is the equation which is satisfied by $P_{n\ell}(r)$, that is, the Hartree function for $\ell = \ell'$. Thus near the origin the solution to the inhomogeneous equation behaves as

$$W_{\ell,\ell'}(r, r_f) \longrightarrow r^{\ell'+1}$$

for $r \to o$; hence the stipulation that the correct starting condition for a large value of r should be the value of $W_{\ell,\ell'}(r, r_f)$ which makes the solution zero at r = o. In the actual calculations the value of $W_{\ell,\ell'}(r_1, r_f)$ was varied over some range until two values were found which enclosed the correct value. For two such values, the solutions $W_{\ell,\ell'}(r, r_f)$ diverge slowly, one to

positive values, the other to negative. The correct starting condition at r_1 was then found by narrowing the interval between the two values which enclose the correct one.

The integration procedure was performed with a program written for the IBM 7090 computer. The numerical method was a modification of the Numerov process for a linear second order differential equation.

B. Polarization Potential for Cesium

The cesium atom, with fifty-five electrons occupying six electron shells, presents a very complicated system for the perturbation calculation. The problem is greatly simplified, however, by the fact that the inner electrons, which are very strongly bound, are perturbed only slightly by the field of the incident particle. Sternheimer, in his calculation of the polarizability of alkali ions, considered only the contribution of the outermost shell to the polarization potential, finding the contribution from the inner electrons to be negligible. In the present calculation, the perturbation of one of the n=4 states was determined and found to be negligible as compared to that of the n=5 states and even less as compared to the contribution from the valence electron. Thus the contribution to the total polarization potential due to the inner electron was neglected in the present calculation; the potential function was determined by the perturbation of the two outermost shells.

Returning now to the notation of Section II for the perturbed wave function $\chi_{l,l'}(\bar{r}, \bar{r}_f)$ the following solutions were obtained.

5-s States

For the two 5-s electrons the radial equation (30), for an S → P solution was solved by the technique described above. The solutions to this equation

in (31), $\chi_{o \to 1}(r, r_f)$ for one particular value of r_f was then integrated numerically for the polarization potential (eq. 19) and multiplied by two. We note that the solution of these equations for some particular r_f gives the contribution of the s-electron to the polarization potential at only one point, namely at the position r_f from the nucleus. Thus in order to obtain the polarization potential for all distances of the perturbing electron from the target atom, the radial equations must be solved and the polarization integrals evaluated for a wide range of values of r_f. In this way the exact shape of the polarization potential can be determined as a function of the distance of the incident particle from the target. Thus the equations were solved in every case for twenty-seven values of the free electron position r_f, and the polarization potential determined at each of these points, in this way the value of V_p was ascertained to the desired degree of accuracy for all positions of the perturbing electron. The unperturbed radial function and the perturbation $U_{5s \to p}$ for one position of the free electron is shown in Fig. 3.

5-p States

There are six electrons in the 5-p state, two with m=o and four with $m=\pm 1$. The m=o states satisfy equation (33) the solution of which determines $\chi_{1 \to o}$. The m=o states also satisfy eq. 35 whose solution $U_{2,o}$ in equation (36) determines $\chi_{1 \to 2}$, a $p \to d$ perturbation. Equation (33) and (35) were solved in the same manner as described above for the 5-s states. The solutions to the differential equation for each value of r_f were subsequently integrated numerically to yield the polarization potential, and multiplied by two since there are two m=o electrons.

For the p-states with $m=\pm 1$ equation (37) was solved similarly yielding

the radial perturbation $U_{2,\pm 1}$ which together with the angular function $Y_2^{\pm 1}(\theta,\phi)$ of equation (38) determines the perturbation $\chi_{1\to 2}$; a $p \to d$ excitation.

6-s State

The valence electron which is in the 6-s state, undergoes an $s \to p$ perturbation similar to the 5-s state, and was treated in the same fashion, the only difference being that the starting values at a large radius r_1 were taken at $r = 25\ a_o$ in the 6-s case, whereas all the n=5 states were started at $r = 14\ a_o$. This was necessary since the valence electron wave function becomes asymtotic much farther out. Also, the polarization integrals were not multiplied by two in this case since there is only one 6s electron. The radial wave function and the perturbation $U_{1,o}$ for r_f=16.0 a_o are shown in Fig. 4.

For comparison the polarization potential as contributed by the valence electron and the total contribution from the n=5 electrons is shown along with the Hartee potential function in Fig. 5. We note that in the region from r=o to $r = 3a_o$ the total contribution from the n=5 shell predomiates, the valence electron contribution being almost negligible. And conversely, in the region $r > 4\ a_o$ the valence electron contribution is larger than that of the inner electrons, the latter becoming negligible rapidly for large r. One also notes that the polarization potential is negligible as compared to that due to the screened nuclear change for small r ($r < 1$) and on the other hand for large r ($r > 6$), the Hartree potential is negligible as compared to the polarization term.

The sum of the contribution from the n =-5 states and that of the valence electron gives the total polarization potential for the electron scattering problem in the present calculation. An estimate of the accuracy of the calculated polarization potential can be made by noting its asymtotic behavior.

We know of course that the value of the polarization potential for large values of r should correspond to that yielded by the dipole polarizability α. Thus we can compare the value of the calculated polarization potential at some large r ($r \sim 25a_o$) to that yielded by the experimentally determined value of α. Using this comparison we find that the polarization potential calculated here corresponds asymtotically to a value of α which is $2 \sim 3$ times the experimental value, depending on which experimental value is used in the comparison.[11] Thus the calculated polarization potential is considerably larger than it should be for large values of r_f. This result is not unexpected however in the light of Sternheimer's work on calculating polarizabilities. Following the argument given by Sternheimer we note that the Hartree wave functions which we have used gives less binding energy than the actual wave functions should give and are thus more external. An increase in the binding of an orbital would decrease the contribution to the polarization potential from that electron. The Hartree-Fock wave functions for an atom or ion have lower energies and are thus more tightly bound than those yielded by the Hartree solutions, hence the use of Hartree-Focks wave function would decrease the calculated polarization potential, a point shown by Sternheimer in his calculation of the polarizability of F^- through the use of both the Hartree and Hartree-Fock solutions.[15] However, even the Hartree-Fock solutions do not yield binding energies as low as the actual wave functions should give, and the corresponding polarization potential is still somewhat too large even in these cases. Sternheimer obtained values of the polarizability which were 1-1.5 times the experimental values for ions whose wave functions were of the Hartree-Fock type and a value which was ~ 3 times the experimental value through the use of the less accurate Hartree Solutions[14,15]. Thus the results obtained here are consistent with these

calculations in the magnitude of the polarization potential. We were, of course, unable to use Hartree-Fock solutions for cesium, though better results would be expected.

We will make one additional observation concerning the results of the present calculation as pertains to the problem of interest to us here. We note that the use of the Hartree wave functions need not affect the shape of the calculated potential function as much as its magnitude for large r. If we consider the contribution of one electron, say the valence electron, to the total interaction we would expect the use of the actual wave function in the radial equation to yield a perturbation similar to that of Fig. 4, with both the unperturbed wave function and its perturbation , lying somewhat more internal. Looking at Fig. 5 we would then expect that the effect on the polarization integrals would simply be a slight change in the position of the maximum of the valence electron contribution, with the shape remaining essentially unchanged. The same argument would also hold for the other electrons. We can expect then that the use of the actual wave functions in calculating the interaction potential would not change the overall shape of the potential function appreciably but would reduce its magnitude somewhat and shift the position of the maximum in the contribution of the various obitals. This is an important consideration in the calculation of scattering cross sections which we are considering here, since we have found that the shape of the polarization potential is very important in the low energy scattering problem. In calculating electron scattering cross sections for the cesium atom we can then simply normalize the calculated polarization potential to the observed asymtotic value expected from the experimental polarizability; a treatment which is similar to that of Stone and Reitz[6].

C. Scattering Cross Sections.

The calculated polarization potential was used in the same method as described in section I, where the term $V_p(r)$ is in this case the calculated potential. The scattering cross sections were obtained by the same method as in I for the same energy regions. The results shown in Fig. 7 were obtained using the polarization potential of Fig. 6 normalized to correspond to a value of 360 a_o^3 for the polarizability α at large r. The cross sections were also calculated using the unnormalized potential function and with a normalization corresponding to $\alpha = 283a_o^3$. In this way the dependence of the cross section on the magnitude of the polarization potential was determined. It was found that the shape of the curve in Fig.7 was essentially unchanged by using different values of α. For the large value of the polarizability the values of the cross sections were increased, and conversely for a smaller value, the curve was lowed for all incident energies.

The cross sections shown in Fig. 7 are seen to agree quite well with the experimental values of Brode for energies greater than 2.5 eV. The values lie somewhat lower than those of Brode, but his experiment included inelastic collisions. The calculated cross sections also agree reasonably well with the very low energy values measured by Chen and Raether,[16] but disagree completely with the various plasma experiments [17] in the region from .075 to .8eV. The work of Stone and Reitz[6] in this region has shown that exchange effects are important for these energies. Since exchange has been neglected here, the calculated cross sections are expected to be somewhat too large in this region.

IV. Conclusions

From the results obtained here and in I we can conclude that a simple model can be used to describe low energy electron scattering by the alkali atoms, where the distortion of the target atom by the incident particle makes the major contribution to the scattering cross sections. From the sensitivity of the cross sections to the cut off parameter of the present model, or more precisely on the position and magnitude of the maximum of the polarization potential, we can appreciate the importance of knowing accurately the contributions to the total scattering interaction due to the distortion of the target atom. Through the use of the adiabotic approximation and the first order perturbation method, this distortion can be determined and the resulting polarization potential calculated for the low energy scattering problem. Our results for the cesium atoms indicate that the inner electrons make an appreciable contribution to the polarization potential for small values of the free electron coordinate r_f, but that the valence electron makes the major contribution in the important region where the Hartree potential becomes negligible. The valence electron contribution exhibits a shape which has the same character as that of the simple model which we have used, that is, the maximum occurs at the approximate position of the last maximum of the unperturbed valence electron wave function. The external nature of the Hartree wave functions, especially that of the valence electron, causes this maximum to lie somewhat too far out. From the results obtained with the model showing the sensitivity of the cross sections to the shape of the polarization potential in this region we can conclude that the use of the simple Hartree wave functions to represent the unperturbed atom in the perturbation calculation can lead

to considerable error in the calculated cross sections in the low energy region.

Finally we conclude that the adiabatic approximation and the perturbation theory of this analysis when applied to a system whose unperturbed wave functions are known with sufficient accuracy, can yield reliable results for the problem of the low energy soft potential scattering of a changed particle.

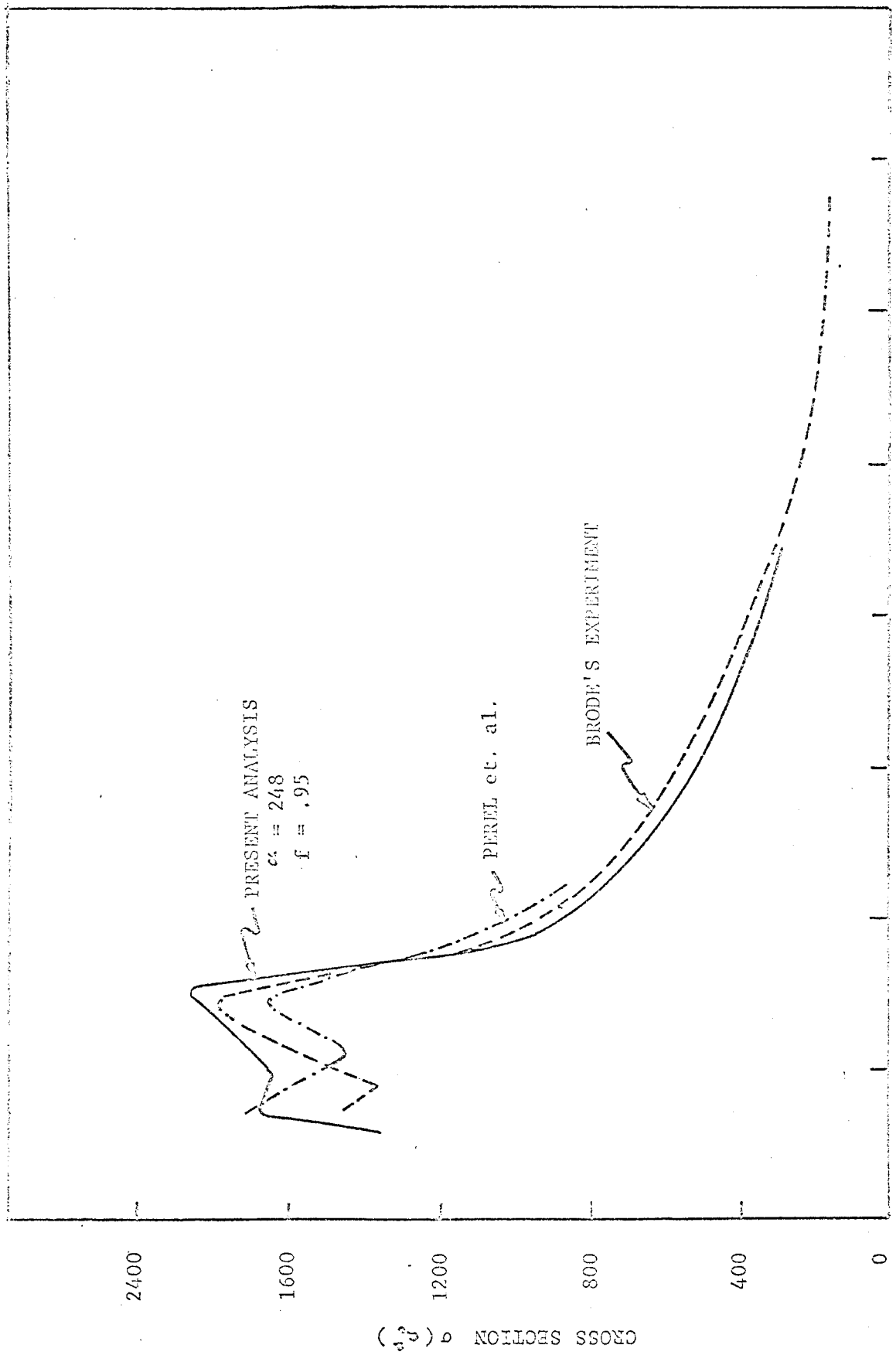

Fig. 1 Total elastic scattering cross sections for potassium yielded by the present model, compared with experimental values of Brode and Perel et. al. ($\alpha = 248$, $kr_o = 4.75$, $k = \sqrt{\epsilon}$).

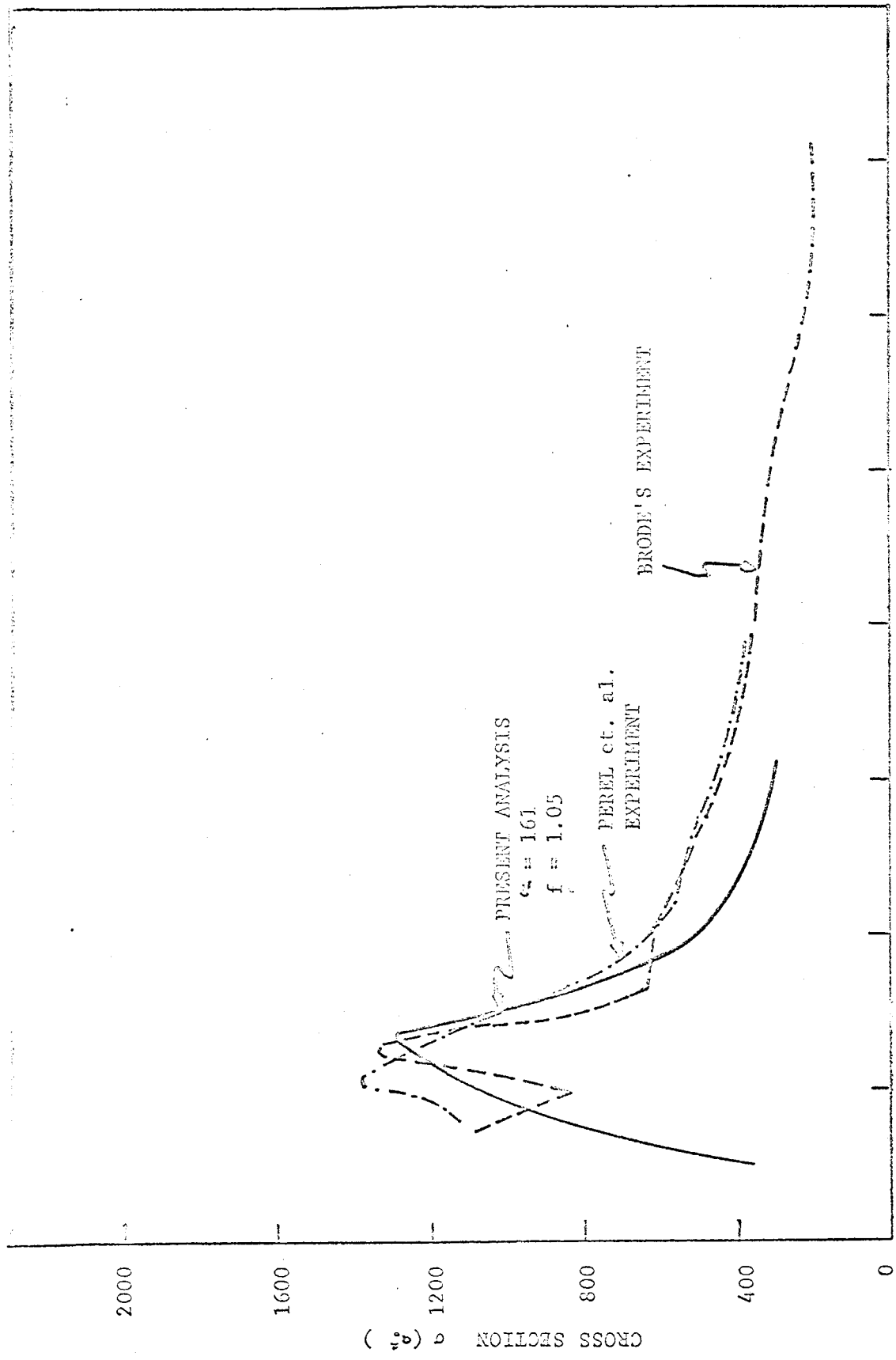

Fig. 2 Total elastic scattering cross sections for sodium from the present model, compared with the result of Brode and of Perel et. al. (α =161, k_o= 3.675).

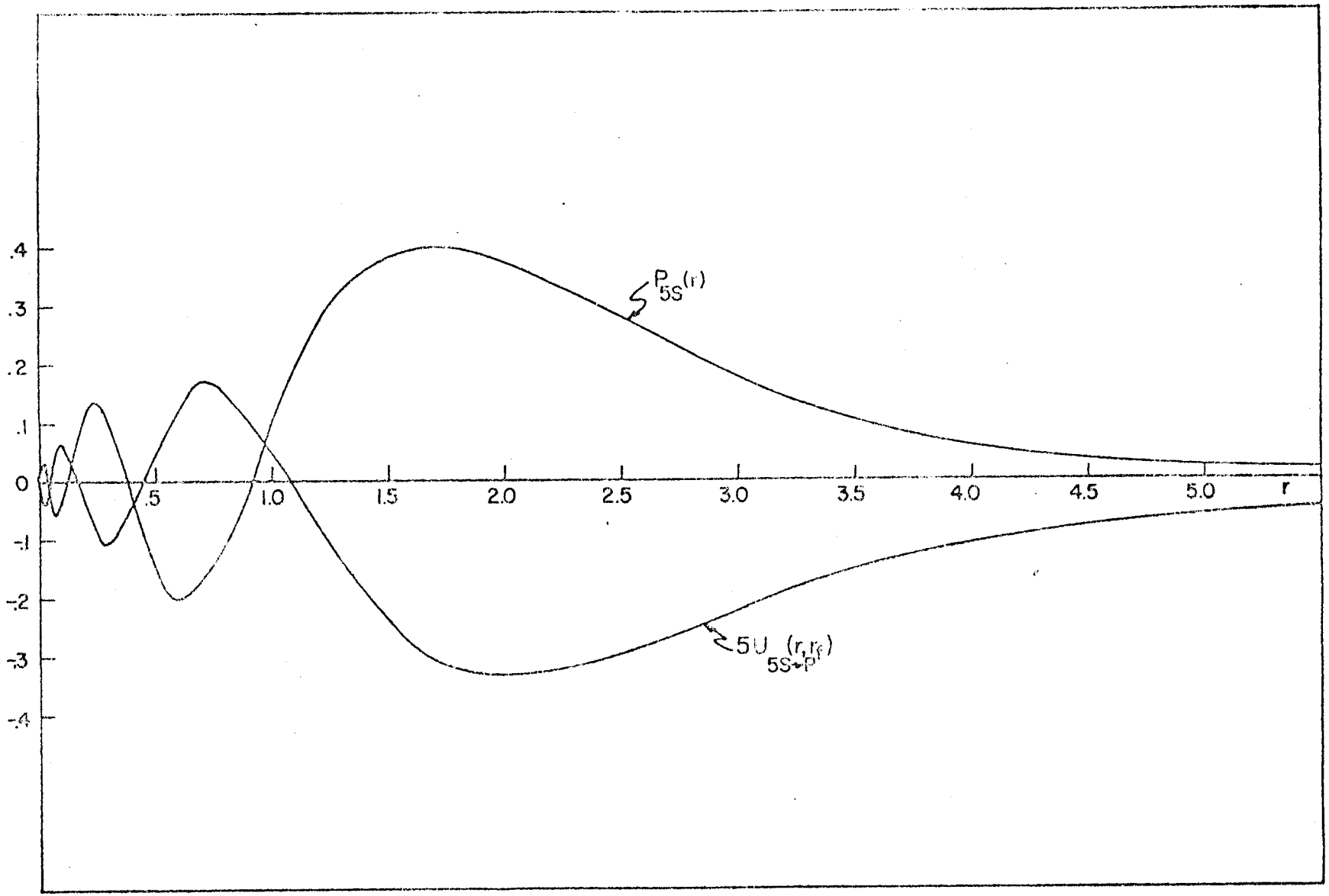

Fig. 3 The unperturbed 5s wave function and the perturbation $5s \to p$ for cesium.

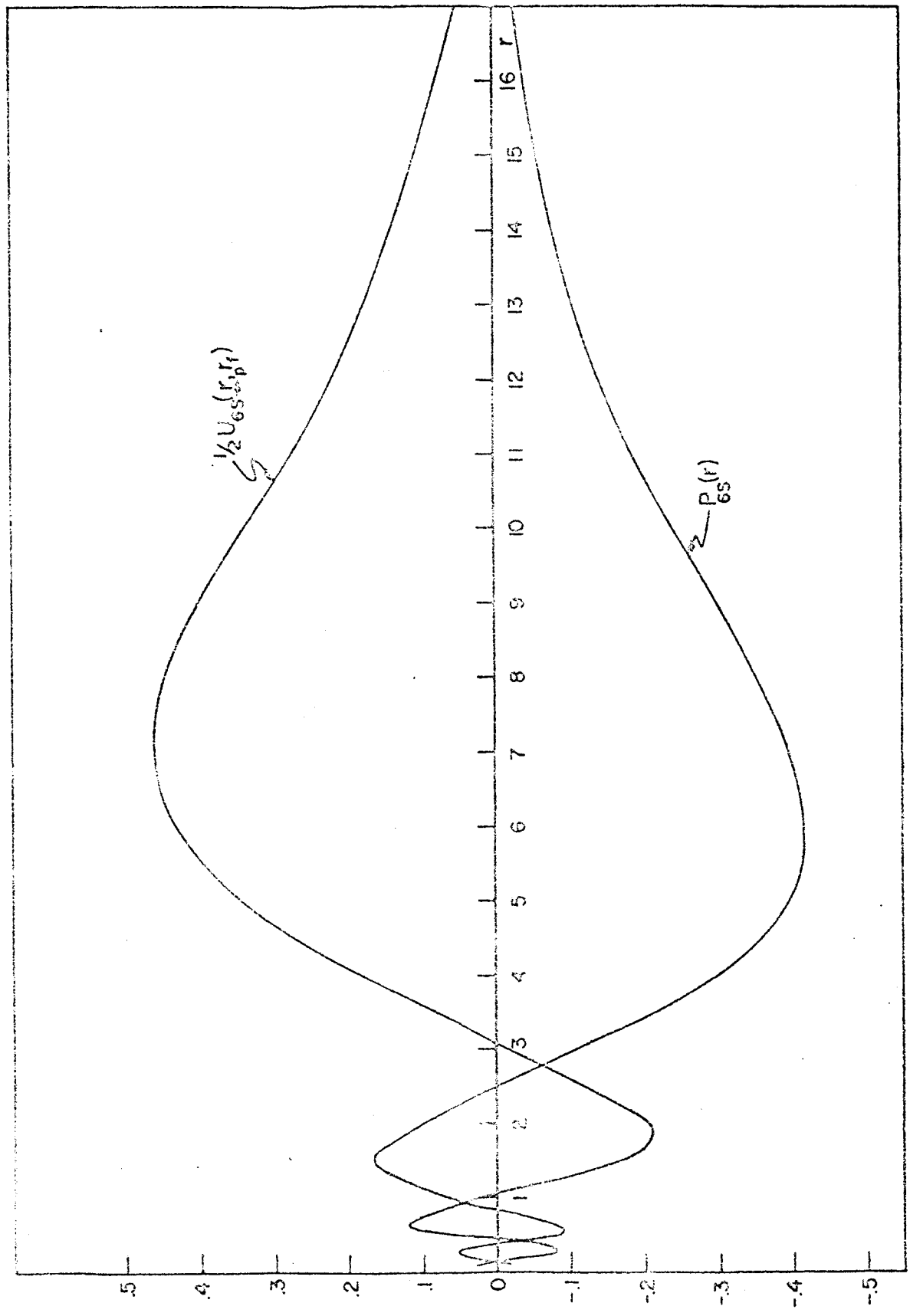

Fig. 1. The 6s wave function and the perturbation 6s → p for cesium.

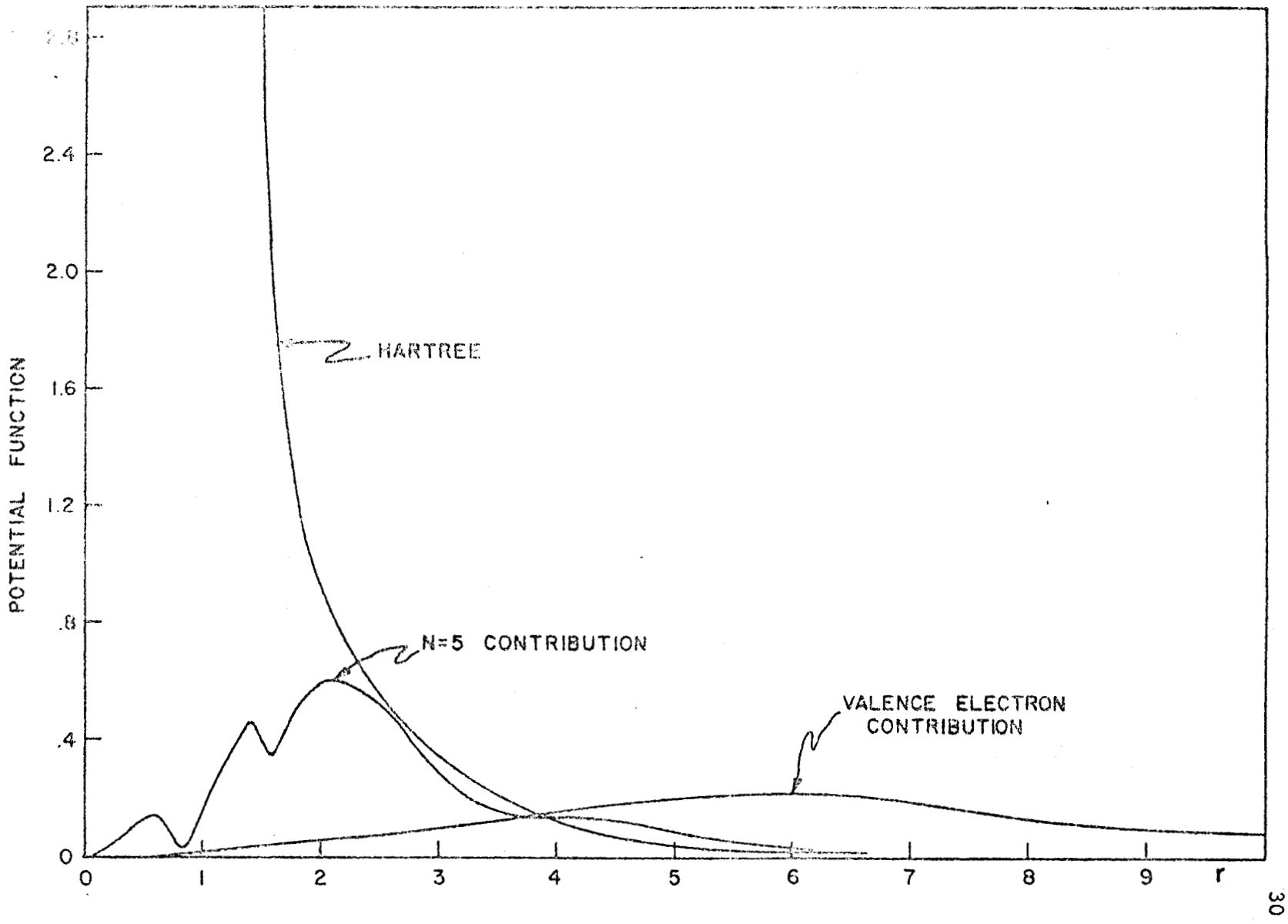

Fig. 5. The Hartree potential function and the polarization potential contributed by the n = 5 and n = 6 electrons.

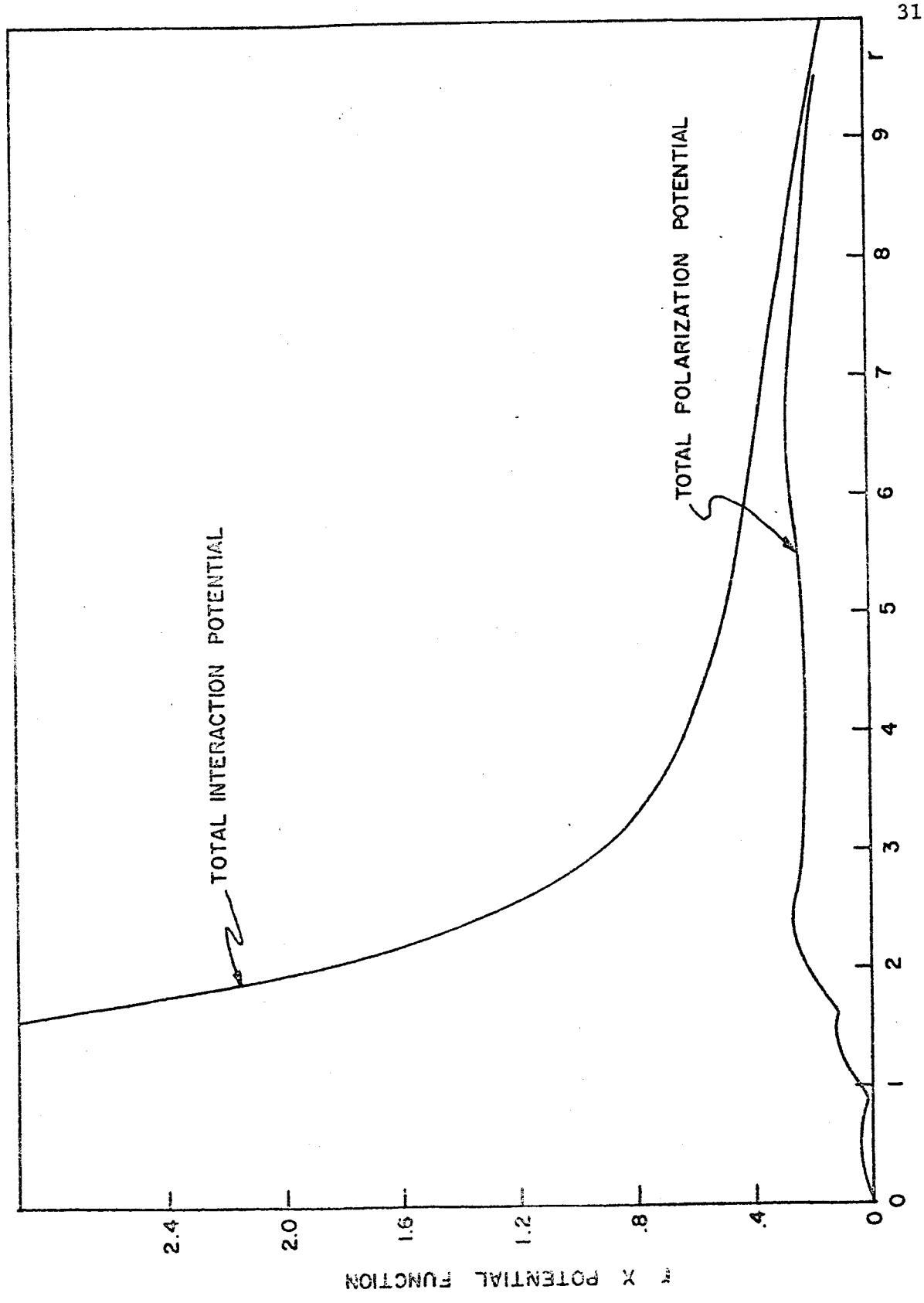

Fig. 6. The total polarization potential $V_p(r)$ and the total interaction potential $V_{II}(r) + V_p(r)$ for cesium. (normalized)

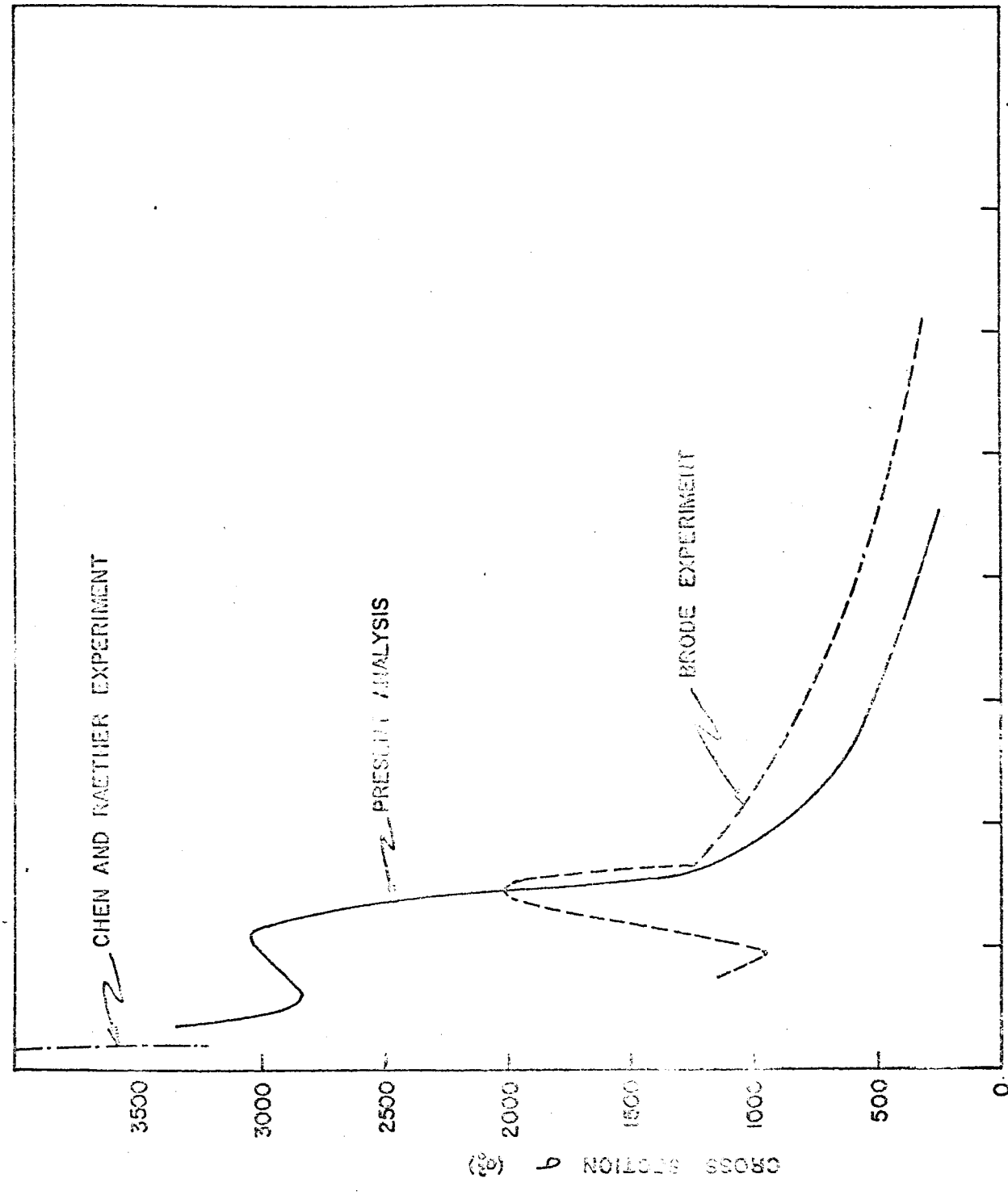

Fig. 7. Total elastic scattering cross section for cesium compared to the experimental values of Brode and of Chen and Raether.

FOOTNOTES

1. W. R. Garrett and R. A. Mann, Phys. Rev., 130, 658 (1963), henceforth referred to as I.

2. L. B. Robinson, Phys. Rev. 127, 2076 (1962).

3. For references see P. G. Burke and K. Smith, Rev. Mod. Phys., 34, 458 (1962).

4. V. D. Ob"Edkov, Soviet Phys.-JETP 16, 463 (1963).

5. J. Calloway, Phys. Rev. 106, 868 (1957).

6. P. M. Stone and J. R. Reitz, Phys. Rev. 131, 2101 (1963).

7. H. Reeh, Z. Naturforsch, 15, 337 (1960).

8. D. R. Hartree, Proc. Roy. Soc. A 143, 506 (1934).

9. J. J. Gibbons, Jr. and J. H. Bartlett, Jr., Phys. Rev. 47, 692 (1935).

10. V. Fock and Mary J. Petrashen, Phys. K. Zeits, D. Sov. J. 6, 368, (1934).

11. A. Salop, E. Pollack, and B. Bederson, Phys. Rev. 124, 1431 (1961).

12. R. B. Brode, Phys. Rev. 34, 673 (1929).

13. J. Perel, P. Englander, and B. Bederson, Phys. Rev. 128, 1148 (1962).

14. R. M. Sternheimer, Phys. Rev. 96, 951 (1954).

15. R. M. Sternheimer, Phys. Rev. 115, 1198 (1959).

16. C. L. Chen and M. Raether, Phys. Rev. 128, 2679 (1962).

17. See R. K. Flavin and R. G. Meyerand, Jr., Symposium on Thermionic Power Conversion, Colorado Springs, May 1962.

Figure Captions

Fig. 1 Total elastic scattering cross sections for potassium yielded by the present model, compared with experimental values of Brode and Perel et. al. (α =248, fr_o =4.75, $k = \sqrt{\epsilon}$).

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Fig. 3 The unperturbed radial 5s wave function and the perturbation 5s $\rightarrow$ p for cesium.

Fig. 4 The 6s wave function and the perturbation 6s $\rightarrow$ p for cesium. r_f= 16.0a_o.

Fig. 5 The Hartree potential function and the polarization potential contributed by the n = 5 and n = 6 electrons for cesium.

Fig. 6 The total polarization potential $V_p(r)$ and the total interaction potential $V_H(r) + V_p(r)$ for cesium (normalized).

Fig. 7 Total elastic scattering cross sections for cesium from the perturbation calculation compared to the experimental values of Brode and of Chen and Raether.